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DEVELOPMENT OF HIGH ENERGY DENSITY
PRIMARY BATTERIES

by

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ABSTRACT

Studies of electrolytes and positive electrode construction for the development of primary CuF_2 -Li batteries were conducted. Solubility of CuF_2 in NaClO_4 -PC electrolyte was not significantly affected by water contamination. Positive electrodes made from thermally decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ gave better shelf life but showed inferior discharge characteristics compared to electrodes made from normal CuF_2 . No beneficial effects from CoF_3 , SbF_3 , and MnF_3 added to CuF_2 were observed. Reducing the concentration of LiClO_4 in propylene carbonate improved the wet shelf life of CuF_2 -Li cells.

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1. SUMMARY

Work was performed toward development of high energy density CuF_2 -Li primary cells. One type of cell is intended for 100-1000 hour discharge rate and presently employs propylene carbonate- LiClO_4 electrolyte. The second cell is intended for the 1 to 10 hour discharge rate and employs methyl formate-lithium perchlorate electrolyte. The experimental work was performed in the following areas:

Electrolyte Systems Studies. Solubility of CuF_2 in solutions of NaClO_4 in propylene carbonate was found to be insensitive to water contamination level. After 360 hours of contact, copper ion concentration in the electrolyte was 19 micro-mols/milliliter.

Solubilities of various salts in propylene carbonate and methyl acetate were studied. The conductivity of 25g of KAsF_6 /100 ml of solvent was $0.11 \text{ ohm}^{-1} \text{ cm}^{-1}$ in methyl acetate and $0.097 \text{ ohm}^{-1} \text{ cm}^{-1}$ in propylene carbonate.

Positive Electrode Studies. Pasted CuF_2 electrodes could not be discharged in MF- LiClO_4 electrolyte when CuF_2 water content was below 0.5 percent. To obtain normal discharge potential (2.9-3.0V) at 10 mA/cm^2 , about 1.5 percent water in the CuF_2 appears necessary.

Electrodes prepared from thermally decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ produced higher cell polarization and lower active material utilization than is obtained with normal CuF_2 , but shelf life was significantly improved. After 30 days of stand at 35°C , best cathodic efficiency was 36 percent compared to 40 percent without stand.

Evaluation of filter mat CuF_2 composition showed good reduction efficiencies (up to 78 percent) with CuF_2 contents as high as 91 percent. Vacuum impregnation with electrolyte improved performance of these cells significantly.

Cell Systems Studies. The effect of adding CoF_3 , SbF_3 , and MnF_3 to CuF_2 on discharge capacity and wet shelf life of CuF_2 -Li cells was studied. Addition of SbF_3 had a detrimental effect, while the other additives did not alter cell performance significantly.

Reduction of LiClO_4 concentration in PC from 20 to 10 grams/100 ml solvent improved wet shelf life of the CuF_2 -Li cells; discharge performance at 0.67 mA/cm² was not affected.

The best performance from CuF_2 -Li cells discharged at the (projected) 100-, 200-, 500-, and 1000-hour rates was obtained at the 200-hour rate (73 percent CuF_2 reduction efficiency). The poorest results were obtained at the 1000-hour rate (23 percent efficiency), while 100- and 500-hour rates gave similar results (58 percent and 47 percent efficiency, respectively).

2. INTRODUCTION

The purpose of this program is the development of high energy density primary battery systems suitable for space flight applications. Two types of batteries, differing in energy density and discharge rate requirements, are being sought: 1) batteries capable of delivering 200 watt hours per pound at the 100-1000 hour discharge rate, and 2) batteries capable of delivering 50 watt hours per pound at the 1 hour discharge rate. For both types of batteries, the CuF_2 -Li couple is being considered. For the low-rate battery, a propylene carbonate-lithium perchlorate electrolyte system is of primary interest, while for the high rate system a methyl formate-lithium perchlorate electrolyte is being investigated. These systems emerged as the most promising at the conclusion of two previous yearly contract periods (NAS 3-2775 and NAS 3-6004).

For the 100-1000 hour battery, the main problem continues to be the limited wet shelf life capability of the system. The electrochemical efficiency of the CuF_2 electrode and the weight ratio of active to inactive materials in the cell also require further improvements in order to increase the potential energy output of the CuF_2 -Li battery.

For the 1-10 hour battery, improvements in discharge capability at the relatively high current densities are required in order to increase the energy density potential of this system. Wet shelf life is not an immediate problem for this battery, since reserve activation may be employed.

The present report describes activity and test results obtained during the fourth quarter of the contract period.

3. DESCRIPTION OF EXPERIMENTAL WORK

3.1. ELECTROLYTE SYSTEMS STUDIES

3.1.1. Solubility of CuF_2 in NaClO_4 -Propylene Carbonate Solutions

The solubility of CuF_2 in LiClO_4 -PC solutions has been studied and reported earlier (see NASA CR-54992, pages 10-17). It was found that the solubility increases with both increasing water content of the system and increasing LiClO_4 concentration. It was believed that the dissolution of CuF_2 takes place thru the double decomposition of LiClO_4 and CuF_2 , i. e.



and that the main driving force for the reaction is the low solubility of LiF in the electrolyte solution.

In order to determine the role of the electrolyte salt, and, particularly, of the alkali metal ion on the solubility of CuF_2 , studies of CuF_2 solubility in solutions of NaClO_4 in propylene carbonate were performed. The procedure employed was similar to that used in earlier tests with LiClO_4 electrolytes, and the concentration of NaClO_4 employed (24g NaClO_4 /100 ml PC) was about equivalent on a molar basis to the 20g/100 ml previously used for LiClO_4 .

The electrolyte solution and CuF_2 were introduced under an argon atmosphere into serum bottles, and water was added with a micro syringe to produce water contamination levels in the range of 70-3000 ppm. The serum bottles were then placed on a laboratory shaker, and copper analyses on small aliquots of solution withdrawn with a syringe were performed periodically.

Results of copper analyses on the solutions after 24, 192, and 360 hours of agitation are presented in Table I, page 5. Karl Fischer analyses were also obtained at various times and are presented, although the figures do not represent the true water contents of the solution because of the presence of copper ions.

In comparing the present CuF_2 solubility results with earlier data for LiClO_4 -PC solutions, no significant effect of water contamination on the solubility of CuF_2 could be observed for the NaClO_4 solutions, while in the LiClO_4 solutions this effect had been strongly pronounced. Although the two solubility tests were not run side-by-side, and may not be directly comparable in some respects (different batches of CuF_2 were employed), the results obtained with NaClO_4 are encouraging. Further work with "non-lithium" electrolytes is in progress, and will include both compatibility and cell performance tests.

TABLE I

SOLUBILITY OF CuF_2 IN NaClO_4 -
PROPYLENE CARBONATE ELECTROLYTE

Propylene Carbonate: MC & B, Lithium dried and redistilled; $\text{H}_2\text{O} = 20$ ppm
 Sodium Perchlorate: G. F. Smith, vacuum dried 18 hours at 110°C ;
 $\text{H}_2\text{O} < 20$ ppm
 Cupric Fluoride: Ozark Mahoning, 0.5% H_2O as $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, untreated
 Electrolyte: 9.2g NaClO_4 /40 ml PC

<u>H_2O Conc. (Calc. init.) $\mu\text{g}/\text{ml}$</u>	<u>Agitation Time (hrs.)</u>	<u>H_2O Conc. (KFA) $\mu\text{g}/\text{ml}$</u>	<u>Copper Conc. (as Cu^{++}) $\mu\text{mols}/\text{ml}$</u>	<u>Solution Color</u>
124	0			
	24	80	10.9	Light grey, green tinge
	192	160	7.8	Light grey, green tinge
	360	220	18.7	Light grey, green tinge
372	0			
	24	340	15.6	Light grey, green tinge
	192	490	10.9	Light grey, green tinge
	360	440	18.7	Light grey, green tinge
1112	0			
	24	950	15.6	Light grey, green tinge
	192	1110	12.5	Light grey, green tinge
	360	920	18.7	Light grey, green tinge
3350	0			
	24	2770	15.6	Grey green
	192	3130	12.5	Grey green
	360	2740	18.7	Grey green
124	0			
	24	80	---	Clear, water white
	192	160	---	Clear, water white
	360	160	---	Clear, water white

3.1.2. Solubility of Electrolyte Salts in Propylene Carbonate and Methyl Acetate

In order to further investigate the possibility of replacing lithium with another alkali metal ion in the electrolyte as a means of reducing CuF_2 decomposition during wet shelf stand of the cells, solubility of several salts in propylene carbonate and methyl acetate was tested. The latter solvent was chosen for the study because of the outstanding stability with respect to lithium obtained in recent tests.

Salts were selected for study both as possible electrolytes and to indicate solubility trends in the two solvents. The specific conductances of the solutions were measured and used as an indication of solubility for the difficultly soluble salts.

The specific conductances of salt solutions in the two solvents are listed in Table II, page 7. The specific conductance of the difficultly soluble salts was taken as a criterion of their solubility in the two solvents. The solubility trend obtained for the fluorides was as expected, with LiF producing the lowest conductivity. The conductivity of KClO_4 in PC was somewhat higher than expected. A relatively high conductivity was recorded for KAsF_6 in propylene carbonate; this appears to be the only salt among those studied which may serve as an electrolyte in both methyl acetate and propylene carbonate.

TABLE II

SPECIFIC CONDUCTANCE OF SALT SOLUTIONS IN
METHYL ACETATE AND PROPYLENE CARBONATE

Temperature: 27.0°C

25g salt added to 100 ml solvent (saturated solutions except as indicated)

<u>Solute</u>	<u>Solvent</u>	<u>Conductivity</u>	<u>Remarks</u>
LiF ¹	MA*	1.04×10^{-7}	
	PC	3.23×10^{-6}	
NaF ⁴	MA	5.38×10^{-7}	
	PC	8.06×10^{-6}	
KF (anh.) ⁴	MA	4.47×10^{-7}	
	PC	3.40×10^{-5}	
LiBr ¹	MA	5.85×10^{-4}	Completely dissolved
	PC	8.78×10^{-3}	
NaBr ³	MA	2.81×10^{-6}	
	PC	3.04×10^{-4}	
KBr ¹	MA	4.35×10^{-7}	
	PC	2.13×10^{-4}	
Li ₂ CrO ₄ ⁴	MA*	5.00×10^{-7}	Solution dark green (sat'd)
	PC	9.70×10^{-5}	
Li ₂ CrO ₄ ²	MA*	7.68×10^{-7}	Solution green
	PC	1.33×10^{-4}	
K ₂ CrO ₄ ²	MA*	1.89×10^{-7}	Solution green
	PC	5.73×10^{-6}	
KClO ₄ ¹	MA*	4.75×10^{-7}	
	PC	1.24×10^{-3}	
KAlF ₆ ⁴	MA	7.70×10^{-7}	
	PC	2.62×10^{-4}	
KAsF ₆ ⁴	MA	10.7×10^{-3}	Completely dissolved
	PC	9.71×10^{-3}	
KCrF ₆ ⁴	MA	2.10×10^{-7}	
	PC	3.33×10^{-6}	
K ₂ TiF ₆ ⁴	MA	5.38×10^{-7}	
	PC	6.33×10^{-6}	
K ₂ ZrF ₆ ⁴	MA	3.41×10^{-7}	
	PC	1.66×10^{-6}	

* Treated methyl acetate (lithium dried and distilled).

¹ Dried for 20 hours at 50°C in vacuum oven.

² Dried for 20 hours at 100°C in vacuum oven.

³ Dried for 60 hours at 100°C in vacuum oven.

⁴ Used as received from manufacturer.

3.2. POSITIVE ELECTRODE STUDIES

3.2.1. Evaluation of Dried CuF_2 in Methyl Formate Cells

A number of discharge tests had previously been performed with pasted CuF_2 electrodes at current densities as high as 15 mA/cm^2 (see page 25, NASA CR-54920). Initial cell polarization at this current density was not excessive, being in the order of 0.8 to 1.0V at -15°C .

A subsequent series of pasted electrodes were constructed in order to evaluate the effect of various conducting materials on cell performance. In attempting to discharge these cells at 10 mA/cm^2 , all cells, including those with the previously developed and tested electrodes, polarized severely. It was concluded that the entire unexpected behavior was caused by the use of a substantially drier CuF_2 in making the pasted electrodes compared to the material used in previous tests. To further investigate this phenomenon, cell tests with several types of CuF_2 were performed, both as received from the manufacturer and after drying treatment at Livingston Electronic Corporation.

Three-plate cells with pasted CuF_2 and sheet lithium electrodes were constructed as previously described. The CuF_2 electrodes were about 0.040" thick and had a theoretical capacity of about 1.0 AH. The paste composition was 100 parts CuF_2 , 10 parts graphite, and 1 part cellulose acetate, with 10 percent ethyl alcohol - 90 percent ethyl acetate as the pasting solution. A glass fiber mat, 0.02" thick, was used for electrode separation. Discharge tests were performed at 300 mA (10 mA/cm^2) at -15°C in LiClO_4 -methyl formate electrolyte (50g salt/100 ml solvent), and the results obtained with the various materials are shown in Table III, page 9.

Performance of the cells can be related directly to the amount of water contained by the CuF_2 used to prepare the electrodes. Material from Lot 7 performed as expected from previous tests when the water content was above one (1) percent. However, after argon stream drying to a water content below 0.3 percent, cell polarization was sufficiently severe to reverse polarity of the cells upon closing of the discharge circuit. Material from Lot 9, which had a water content of about 0.4 percent as received from the manufacturer, gave equally poor results.

The above results appear to indicate that completely dehydrated CuF_2 is too insoluble in the LiClO_4 -MF electrolyte to allow discharge at 10 mA/cm^2 . A water content of one (1) percent seems to be required for discharge at the 1-10 hour rate. For a reserve-activated system, this water content does not appear to be prohibitively high.

TABLE III

DISCHARGE PERFORMANCE OF DRIED CuF_2 IN MF- LiClO_4 CELLSCurrent Density: 10 mA/cm²

Cell No.	CuF_2 Treatment	% H_2O by X-ray	Dry paste Wt., gms.	CuF_2 Capacity, AH	Open Circuit Potential	Discharge Potential		Capacity to 2.0VF, AH	Cathodic Eff., %
						Initial	Average		
A-1	Lot 9B, untreated	0.4	2.40	.982	3.55	1.90*	2.72	.455	46.3
A-2	Lot 9B, untreated	0.4	2.62	1.08	3.50	*	---	.051	4.7
A-3	Lot 9B, untreated	0.4	2.67	1.11	3.56	*	---	---	---
B-1**	Lot 7, 16 hrs. vacuum, room temp.	1.5	2.54	1.05	3.57	2.71	2.73	.732	69.7
B-2**	Lot 7, 16 hrs. vacuum, room temp.	1.5	2.25	0.910	3.54	3.00	2.75	.615	67.7
B-3**	Lot 7, 16 hrs. vacuum, room temp.	1.5	2.17	0.873	3.55	2.97	2.69	.555	63.7
C-1	Lot 7, 16 hrs. vacuum, 70°C	1.2	2.28	0.925	3.50	2.56	2.68	.615	66.5
C-2	Lot 7, 16 hrs. vacuum, 70°C	1.2	2.30	0.934	0.02	Rev.	---	---	---
C-3	Lot 7, 16 hrs. vacuum, 70°C	1.2	2.44	1.00	3.55	2.91	2.70	.663	66.3
D-1	Lot 7, 23 hrs. argon sweep, 152°C	<0.3	2.35	0.958	3.56	Rev.	---	---	---
D-2	Lot 7, 23 hrs. argon sweep, 152°C	<0.3	2.30	0.934	3.57	Rev.	---	---	---
D-3	Lot 7, 23 hrs. argon sweep, 152°C	<0.3	2.37	0.967	3.57	Rev.	---	---	---

*Voltage dropped rapidly below 2.0V cutoff

**100-200 microns

3.2.2. Evaluation of Thermally Decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in Methyl Formate Cells

The thermal decomposition products of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ were identified in earlier X-ray studies (see NASA CR-54992, pages 20 to 22), and were found to consist mainly of hydroxy fluorides CuOHF and $\text{CuOHF} \cdot \text{CuF}_2$ as well as an unidentified compound with a major peak intensity at 4.15 Å. These materials appeared to be relatively insoluble in the LiClO_4 electrolyte solutions, and have an equivalent weight which is slightly lower than that of normal CuF_2 . Thus, the $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ decomposition products were of interest as possible cathodic reactants, and the discharge performance of thin pasted electrodes made with $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and its decomposition products was studied in positive-limited cells with lithium anodes and LiClO_4 -methyl formate electrolyte.

Materials used for the preparation of pasted electrodes included untreated $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, a mixture of 95 percent CuF_2 (0.5 percent H_2O) and 5 percent $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, and thermal decomposition products of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$.

The pasted positive electrodes, and 3-plate test cells were prepared as described in Section 3.2.1. Discharge tests were performed as usual at 10 mA/cm² and -15°C; results of the discharge tests are tabulated in Table IV, page 11.

The CuF_2 - $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ mixture produced electrodes having about the same discharge characteristics as have been observed with electrodes made from CuF_2 as received from the manufacturer and having an equivalent total water content (ca. 2 percent). Electrodes made from 100 percent $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ gave similar discharge potential and electrochemical efficiency as the CuF_2 - $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ mixture. However, cells built from electrodes containing the $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ decomposition products could not be discharged at 10 mA/cm² (almost immediate polarity reversal occurred at this current density).

The above results further demonstrate that (1) water in the range of 1-2 percent may be necessary for rapid discharge of CuF_2 , and (2) the source of water is of no importance—it may be present as an impurity in the original CuF_2 , or it may be added in the form of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$.

TABLE IV

PERFORMANCE OF $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ AND DECOMPOSITION PRODUCTS
WITH Li ANODES IN $\text{LiClO}_4\text{-MF ELECTROLYTE}$

Cell No.	Active Material	Dry paste Wt., gms.	CuF ₂ Capacity, AH	Open Circuit Potential	Discharge Potential		Capacity to 2.0VF AH	Cathodic Eff., %
					Initial	Average		
A-1	95% CuF ₂ , 5% CuF ₂ ·2H ₂ O	3.06	1.23	3.61	2.91	2.69	0.845	68.7
A-2	95% CuF ₂ , 5% CuF ₂ ·2H ₂ O	2.46	0.998	3.61	2.98	2.76	0.702	70.4
A-3	95% CuF ₂ , 5% CuF ₂ ·2H ₂ O	2.62	1.07	3.61	2.54	2.42	0.475	44.4
B-1	CuF ₂ ·2H ₂ O, 15 hrs. at 150°C in sealed oven	3.13	---	3.61	---*	---	---	---
B-2	CuF ₂ ·2H ₂ O, 15 hrs. at 150°C in sealed oven	2.93	---	3.61	1.41	---	---	---
B-3	CuF ₂ ·2H ₂ O, 15 hrs. at 150°C in sealed oven	3.13	---	3.60	---*	---	---	---
C-1	CuF ₂ ·2H ₂ O, 20 hrs. at 185°C, argon sweep	2.32	---	3.56	Reverse	---	---	---
C-2	CuF ₂ ·2H ₂ O, 20 hrs. at 185°C, argon sweep	2.21	---	3.57	Reverse	---	---	---
C-3	CuF ₂ ·2H ₂ O, 20 hrs. at 185°C, argon sweep	2.73	---	3.57	Reverse	---	---	---
D-1	CuF ₂ ·2H ₂ O, no treatment	2.89	1.01	1.50	Reverse	---	---	---
D-2	CuF ₂ ·2H ₂ O, no treatment	2.55	0.89	3.63	2.94	2.76	0.520	66.9
D-3	CuF ₂ ·2H ₂ O, no treatment	2.77	0.97	3.63	2.94	2.76	0.558	65.3

*Erratic

3.2.3. Evaluation of Conductors in Pasted CuF_2 Electrodes

To evolve CuF_2 electrodes for high energy density, relatively high discharge rate cells, the ratio of active to inactive material in the electrodes must be high.

In electrodes operating at relatively high current densities, this may not be achieved at the expense of conductivity of the matrix. Thus, additives which lend good conductance, when added in small concentrations, are desired for such electrodes.

Three conductive materials were compared in cell tests with Dixon air spun graphite, which has been used in most cell tests to date. The conductors evaluated were Conductex SC and SA-40-220 (Columbian Carbon Company) and alkaline battery type nickel flake (Electric Storage Battery Company). Conductex SC is a carbon black used for producing conductive film while SA-40-220 is being developed for battery applications.

Pasted CuF_2 electrodes were prepared as described in the previous sections. The mix composition was 20 grams CuF_2 (Lot 7, H_2O content ca. 1.5 percent), 1 gram conductive material, and 0.2 gram cellulose acetate. After blending the dry components in a micronizer blender, pastes were prepared using a 10 percent alcohol - 90 percent ethyl acetate pasting solvent, and pasted onto expanded metal. After vacuum drying of the electrodes, three-plate cells with two lithium electrodes and glass fiber separation were assembled, activated with LiClO_4/MF electrolyte (50g salt/100 ml solvent), and discharged at 10 mA/ cm^2 at -15°C . Construction data and discharge results for the cells are listed in Table V, page 13, and voltage-time data for the best of the three cells in each group are plotted in Figure 1, page 14.

In this test series, the cells which had carbon black in the CuF_2 paste mix gave better discharge performance than those with either graphite or nickel flake at the same concentration. Cell performance replication was comparatively poor, except for cells which had nickel flake additive. Also, the poor performance of cells having graphite conductor has not been characteristic to this paste composition in earlier tests (see NASA CR-54920, pages 22 and 23). However, the performance of the best cells with carbon black additive was quite encouraging, with CuF_2 reduction efficiencies as high as 65 percent at the ca. 2 hour discharge rate. Since the active material in these electrodes is in the order of 80-90 percent including the weight of the silver grid, high energy densities should be possible in this construction even at the relatively short discharge times.

TABLE V

CONDUCTIVE MATERIAL EVALUATION

Discharge Current: 300 mA/cell (10 mA/cm²)
 Temperature: -15°C

Cell No.	Conductive Material*	Dry paste Wt., gms.	CuF ₂ Capacity, AH	Open Circuit Potential	Discharge Potential		Capacity to 2.0VF, AH	Cathodic Eff., %
					Initial	Average		
A-1	Conductex SC ¹	2.33	.997	3.56	2.86	2.70	.616	61.8
A-2	Conductex SC	2.75	1.205	3.54	2.95	2.71	.777	64.4
A-3	Conductex SC	2.60	1.131	3.55	2.06	2.08	.087	7.7
B-1	SA-40-220 ²	2.54	1.101	3.53	3.09	2.74	.717	65.0
B-2	SA-40-220	2.45	1.056	3.53	3.09	2.74	.693	65.6
B-3	SA-40-220	2.10	.931	3.53	2.89	2.61	.516	55.5
C-1	Graphite ³	2.60	1.131	3.45	Rev.	---	---	---
C-2	Graphite	2.59	1.126	3.55	2.64	2.64	.087	7.7
C-3	Graphite	2.70	1.180	3.54	2.66	2.32	.351	29.7
D-1	Ni Flake ⁴	3.00	1.330	3.52	2.96	2.65	.562	48.6
D-2	Ni Flake	2.71	1.185	3.51	2.92	2.57	.567	48.0
D-3	Ni Flake	3.00	1.330	3.46	3.02	2.62	.642	48.2

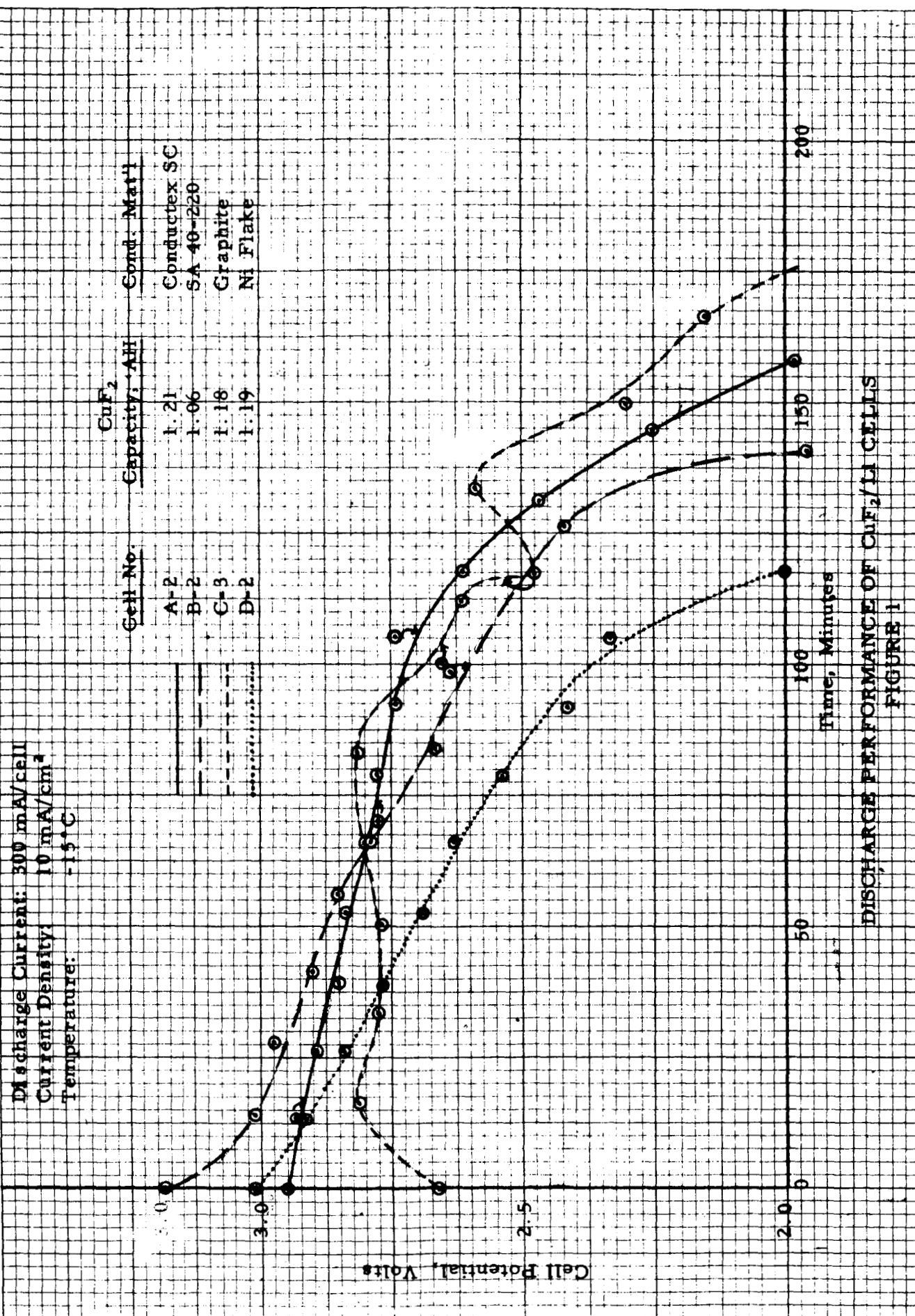
* 5 grams/100 grams CuF₂

¹ Columbian Carbon Company

² Columbian Carbon Company

³ Dixon Airspun

⁴ E. S. B. Company, Alkaline Battery Division



3.2.4. Evaluation of Thermally Decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in Propylene Carbonate Cells

Drying of CuF_2 by various methods has been investigated previously in attempting to improve the shelf life of activated CuF_2 -Li cells. Since the water is known to exist as $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$, thermal decomposition of this compound was also studied. After some indications of low solubility of the thermal decomposition products in the LiClO_4 -propylene carbonate electrolyte were obtained, cell tests with decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ electrodes were initiated.

The positive active material was prepared by heating $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ in a tube swept by argon for 57 hours at 180-188°C. The resulting material showed a 23 percent weight loss from the dihydrate, and the composition was shown by X-ray analysis to be

Unknown Material*	63%
CuOHF	28%
$\text{CuOHF} \cdot \text{CuF}_2$	<u>12%</u>
TOTAL	103%

*Major peak intensity at 4.15 Å.

Filter mat electrodes were prepared by the methods described in previous reports (see NASA CR-54803, pages 67-72). The mix composition was

Active Material	104
Graphite	14
Paper Fiber	7.

Twelve 3-plate CuF_2 -Li test cells were constructed and activated with 15g LiClO_4 /100 ml propylene carbonate electrolyte (water 50 ppm by Karl Fischer analysis). Groups of four cells were assembled and sealed (with cell terminals protruding) in polyethylene containers measuring 4 x 4 x 3 inches. Four cells were put on discharge thru 200-ohm loads at 35°C, while the remaining cells were discharged under the same conditions after open circuit stand periods of 9 and 30 days at 35°C.

Discharge data for the cells are summarized in Table VI, page 17, and cell open circuit potentials during stand are given in Table VII, page 18. Voltage-time data during discharge and open circuit stand have been plotted for the last cell in each group in Figures 2 and 3, pages 19 and 20.

In comparison to the normal CuF_2 , the decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ produced higher cell polarization at the 200-ohm loads. All cells, except Cell #1, fell in potential to below 2.5V after 4 hours of discharge. Because of the distinctly green electrolyte color in Cell #1, it was suspected that this cell had been contaminated with water, possibly thru the use of an improperly dried hypodermic syringe. The positive active material utilization efficiency was likewise reduced to about one-half of that obtainable from normal CuF_2 . Open circuit potential during stand, and capacity after stand were significantly better, however. The average discharge potential of cells after 30 days of stand was higher than for cells which had no stand, with only a slight reduction in active material utilization.

The decomposed $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ appears to be reducible in the LiClO_4 -propylene carbonate electrolyte, but its low solubility does not permit the normal 200-ohm discharge. The significantly better shelf life observed with this material can likewise be explained in terms of its lower solubility in the electrolyte solution. Further studies on this material are required to fully evaluate its properties and possible advantages over normal CuF_2 as the active material of the cell.

TABLE VI

PERFORMANCE OF DECOMPOSED $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$
WITH LI ANODES IN $\text{LiClO}_4\text{-PC ELECTROLYTE}$

Stand Temperature: $+35^\circ\text{C}$

Discharge Condition: $+35^\circ\text{C}$, 200 Ω

Cell No.	Theo. CuF_2 Capacity, AH*	Initial O. C. Voltage	O. C. Stand Time, days	O. C. Voltage after stand	Discharge Time, 2.0VF, hrs.	Average Discharge Potential, Volts		AH to 2.0VF	Percent Efficiency
						Potential,	Volts		
1	3.96	3.52	0	---	129	2.85	1.84	1.84	47
2	4.05	3.52	0	---	136	2.33	1.58	1.58	39
3	4.33	3.52	0	---	148	2.32	1.72	1.72	40
4	3.96	3.52	0	---	119	2.30	1.37	1.37	35
5	4.08	3.52	9	3.42	<30	---	---	---	---
6	3.90	3.52	9	3.56	108	2.20	1.19	1.19	30
7	3.98	3.52	9	3.56	108	2.21	1.19	1.19	30
8	3.23	3.52	9	3.54	96	2.18	1.05	1.05	32
9	4.03	3.52	30	3.33	98	2.63	1.29	1.29	32
10	3.79	3.52	30	3.52	<12	---	---	---	---
11	3.97	3.53	30	3.33	104	2.77	1.44	1.44	36
12	3.73	3.52	30	3.53	43	2.27	.44	.44	13

17

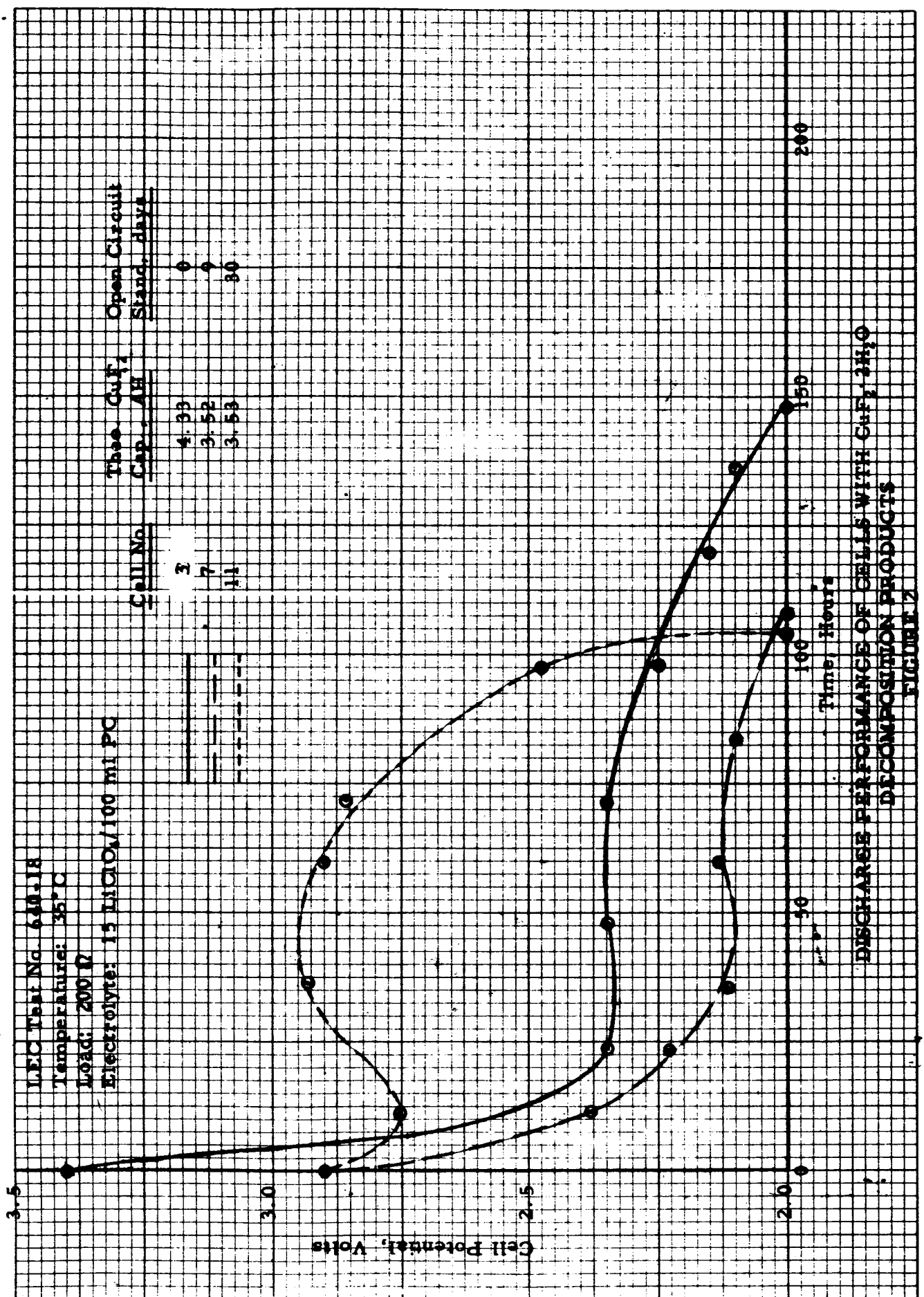
* The equivalent weight for the material is assumed to be the same as for CuF_2 .

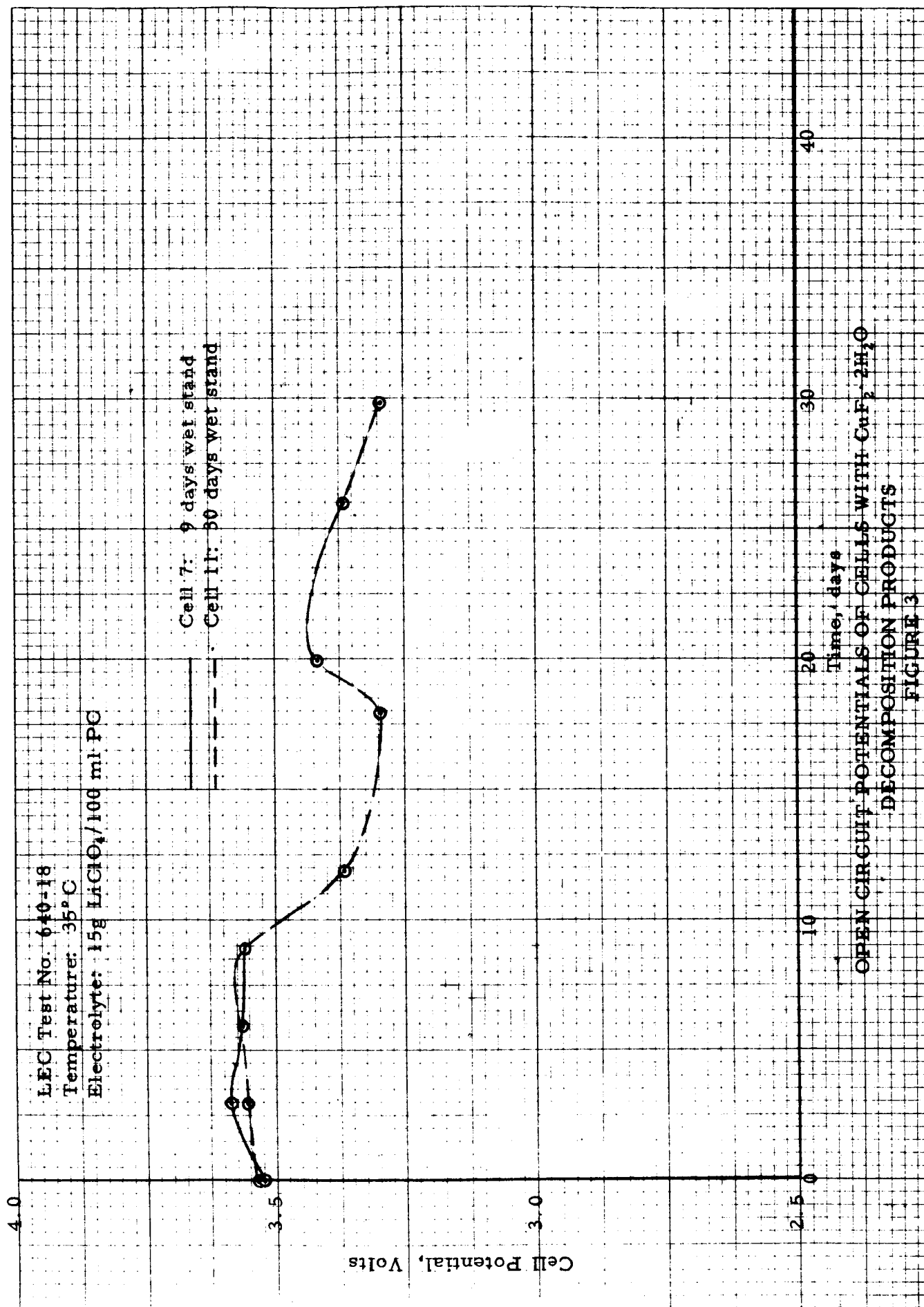
TABLE VII

OPEN CIRCUIT POTENTIALS OF DECOMPOSED $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$
VS. LITHIUM IN LiClO_4 -PC ELECTROLYTE

Temperature: 35°C

Cell No.	0 day	3 days	4 days	5 days	6 days	7 days	9 days	11 days	12 days	13 days	18 days	19 days	20 days	25 days	26 days	30 days
5	3.52	3.59	3.58	3.58	3.57	3.56	3.42									
6	3.52	3.59	3.58	3.57	3.56	3.56	3.56									
7	3.52	3.59	3.58	3.58	3.57	3.56	3.56									
8	3.52	3.58	3.57	3.56	3.55	3.54	3.54									
9	3.52	3.59	3.58	3.57	3.56	3.55	3.55	3.52	3.51	3.51	3.50	3.50	3.45	3.35	3.37	3.33
10	3.52	3.59	3.58	3.57	3.57	3.56	3.56	3.55	3.53	3.53	3.50	3.52	3.52	3.53	3.55	3.52
11	3.53	3.60	3.59	3.58	3.57	3.56	3.56	3.42	3.37	3.36	3.30	3.40	3.42	3.45	3.37	3.33
12	3.52	3.58	3.57	3.56	3.56	3.55	3.55	3.54	3.53	3.53	3.50	3.52	3.52	3.52	3.52	3.53





3.2.5. Copper Fluoride Filter Mat Composition Study

Further composition evaluation was performed for the CuF_2 filter mat electrodes during the past quarter. Previous tests had indicated that substantially higher CuF_2 contents than the 82.5 percent commonly used may be satisfactory, but discharge results showed a large degree of variation between replicate cells. It appeared that poor wetting of the cathode matrix with the electrolyte solution may be causing the non-uniformity in cell performance. This condition was more evident in cells in which a high ratio of graphite to paper fiber was used.

In the present test series, four test cells for each positive electrode composition were constructed and tested. The filter mat electrodes were prepared as described previously, and the graphite and paper pulp concentrations were varied over the range of 4-16 and 2-8 grams/100g CuF_2 , respectively. The test cells had the usual sandwich construction with one filter mat CuF_2 electrode, and two lithium slab electrodes separated by 0.03 in. microporous rubber. After addition of 15g LiClO_4 /100 ml PC electrolyte, two cells in each group were placed in a desiccator and maintained under vacuum until no further gassing from the electrodes and separators could be observed. The vacuum was then released, and the electrolyte levels in the cells were adjusted to the previous height. The remaining two cells in each group were filled by the normal procedure. Discharges were then started at a constant current of 21 mA and a temperature of 35°C. A summary of construction and discharge data for the cells is given in Table VIII, page 22 (electrolyte volume for cells 1-1 thru 3-4 was not obtained because leaks in the polyethylene envelopes caused an undetermined amount of loss during filling.).

Vacuum impregnation improved cell performance significantly for the higher CuF_2 content mixes (Cells 1-1 thru 2-4). For the cells having the higher additive levels, no apparent benefit from vacuum impregnation resulted.

Considerable variation in CuF_2 reduction efficiency among replicate cells was again encountered over the entire composition range. The highest efficiencies were obtained with cells having the highest graphite content (16g/100g CuF_2). However, increasing the paper fiber content appeared to affect the performance adversely, which may be an indication that this material (S & S filter paper pulp, acid washed) causes some contamination in the cell. It may be possible to replace some of the filter paper pulp with other, preferably conductive, fibrous material (such as graphite fibers).

A variance analysis of the cell performance data is presented in Appendix I.

TABLE VIII

EFFECT OF ADDITIVE CONCENTRATION
ON PERFORMANCE OF CuF₂ ELECTRODES

(LEC Test #640-7A)

Cell No.	Grams		% CuF ₂ in mix	Theo. CuF ₂ Capacity, AH	Electrolyte Volume, cc	Time to 2.5VF, hrs.	Average Potential to 2.5VF, Volts	Capacity to 2.5VF, AH	CuF ₂ Reduction Efficiency, %
	Graphite	Additive/100g CuF ₂ Paper Fiber							
1-1	4	2	94	3.80	---	0	---	---	---
1-2	4	2	94	3.68	---	0	---	---	---
1-3	4	2	94	4.08	---	138 ¹	2.73	2.90	71
1-4	4	2	94	3.96	---	138 ¹	2.85	2.90	73
2-1	8	2	91	3.82	---	109	2.82	2.29	60
2-2	8	2	91	4.03	---	150	3.00	3.15	78
2-3	8	2	91	3.96	---	96	2.94	2.02	51
2-4	8	2	91	3.92	---	56	2.78	1.18	30
3-1	16	2	85	4.00	---	150	3.08	3.15	79
3-2	16	2	85	3.36	---	134	3.01	2.82	84
3-3	16	2	85	4.16	---	160	2.97	3.36	81
3-4	16	2	85	3.68	---	119	3.00	2.50	68
4-1	4	4	93	3.83	8.8*	84 ²	2.59	1.76	46
4-2	4	4	93	4.15	7.7*	<12	---	---	---
4-3	4	4	93	3.92	6.5	89	2.91	1.87	48
4-4	4	4	93	3.97	6.5	128	2.87	2.69	68
5-1	8	4	89	3.85	7.5*	138	2.89	2.90	75
5-2	8	4	89	4.30	7.7*	90	2.83	1.89	44
5-3	8	4	89	4.12	6.5	165	2.99	3.27	79
5-4	8	4	89	3.57	6.5	135	2.92	2.84	80

¹ Load voltage below 2.5V for first 12 hours.

² Load voltage below 2.5V at 24 hours.

* Vacuum impregnated.

TABLE VIII (Continued)

EFFECT OF ADDITIVE CONCENTRATION
ON PERFORMANCE OF CuF_2 ELECTRODES

(LEC Test #640-7A)

Cell No.	Grams Additive/100g CuF_2 <u>Graphite Paper Fiber</u>	% CuF_2 in mix	Theo. CuF_2 Capacity, AH	Electrolyte Volume, cc	Time to 2.5VF, hrs.	Average Potential to 2.5VF, Volts	Capacity to 2.5VF, AH	CuF_2 Reduction Efficiency, %
6-1	16	83	4.52	9.6*	165	2.93	3.22	71
6-2	16	83	3.72	8.2*	0	---	---	---
6-3	16	83	3.28	6.5	139	2.91	2.92	89
6-4	16	83	3.21	6.5	123	3.01	2.58	81
7-1	4	89	3.69	6.0*	71	2.89	1.49	40
7-2	4	89	3.78	6.0*	92	2.84	1.93	51
7-3	4	89	4.45	7.0	138 ¹	2.89	2.84	64
7-4	4	89	3.85	6.6	95 ¹	2.73	1.99	52
8-1	8	86	4.38	7.0*	94 ²	2.75	1.97	45
8-2	8	86	4.45	7.0*	95	2.93	1.99	45
8-3	8	86	3.62	6.5	98	3.01	2.06	57
8-4	8	86	4.18	7.0	98	2.98	2.06	49
9-1	16	81	4.18	7.5*	89	2.87	1.87	45
9-2	16	81	4.27	7.5*	106	3.09	2.23	56
9-3	16	81	3.96	7.0	<36	---	---	---
9-4	16	81	4.07	6.5	45	2.90	0.95	23

¹ Load voltage below 2.5V for first 12 hours.

² Load voltage below 2.5V at 24 hours.

* Vacuum impregnated.

3.3. CELL SYSTEMS STUDIES

3.3.1. Evaluation of CoF_3 , SbF_3 , and MnF_3 as Additives to CuF_2 Electrode

Evaluation of additives to filter mat CuF_2 electrodes was undertaken in order to study methods for improving shelf life of CuF_2 -Li cells having propylene carbonate electrolyte. Since it has been demonstrated that presence of water is detrimental to shelf life of the cells, materials which are known to react with water were selected for addition to CuF_2 during preparation of the electrodes. It was hoped that these additives would decompose the contamination water released by CuF_2 during stand, thus reducing its solubility in the electrolyte solution and improving capacity retention of the cells.

The additives selected for testing were CoF_3 and MnF_3 at a concentration of 4 grams/100 grams of CuF_2 , and SbF_3 at 6 grams/100g CuF_2 (the concentration of additive being roughly proportional to its molecular weight). These were added to CuF_2 prior to jar milling with graphite under heptane. The filter mat composition for construction of the electrodes was 100 parts CuF_2 , 14 parts graphite, and 7 parts paper fiber, plus additive. Electrodes were prepared as described previously by pressing 1.5 x 1.5 in. sections of the filter mat onto expanded silver and removing the residual heptane by vacuum drying. Three electrode cells with outside lithium electrodes and MPR separation were constructed and tested for performance with LiClO_4 -PC electrolyte (15 grams salt/100 ml solvent).

Six cells for each type of additive, and six having no additive were constructed and tested. Two cells from each group were discharged thru 200-ohm at 35°C after one (1) day open circuit stand at 35°C; the remaining cells were discharged after stand periods of 8 and 14 days at 35°C.

Construction and discharge data for the cells are summarized in Table IX, page 25, while the open circuit potentials of cells during stand are listed in Table X, page 26. Voltage-time data for the best cell in each group are presented in Figures 4 to 7, pages 27 to 30.

Addition of SbF_3 had a clearly detrimental effect on both discharge capacity and capacity retention after stand. Addition of CoF_3 and MnF_3 appeared to have no significant effect on the characteristics of the cells. These cells suffered an average capacity loss of about 50 percent after 8 days stand at 35°C. After 14 days at the same temperature, only half of the cells had retained any capacity above a load potential of 2.5 volts. Inspection of the cells after discharge indicated that dissolution of the CuF_2 had taken place, which still appears to be the main cause of capacity decay during stand.

TABLE IX

DISCHARGE PERFORMANCE OF CuF_2 -Li CELLS CONTAINING ADDITIVES
(LEC 640-15)

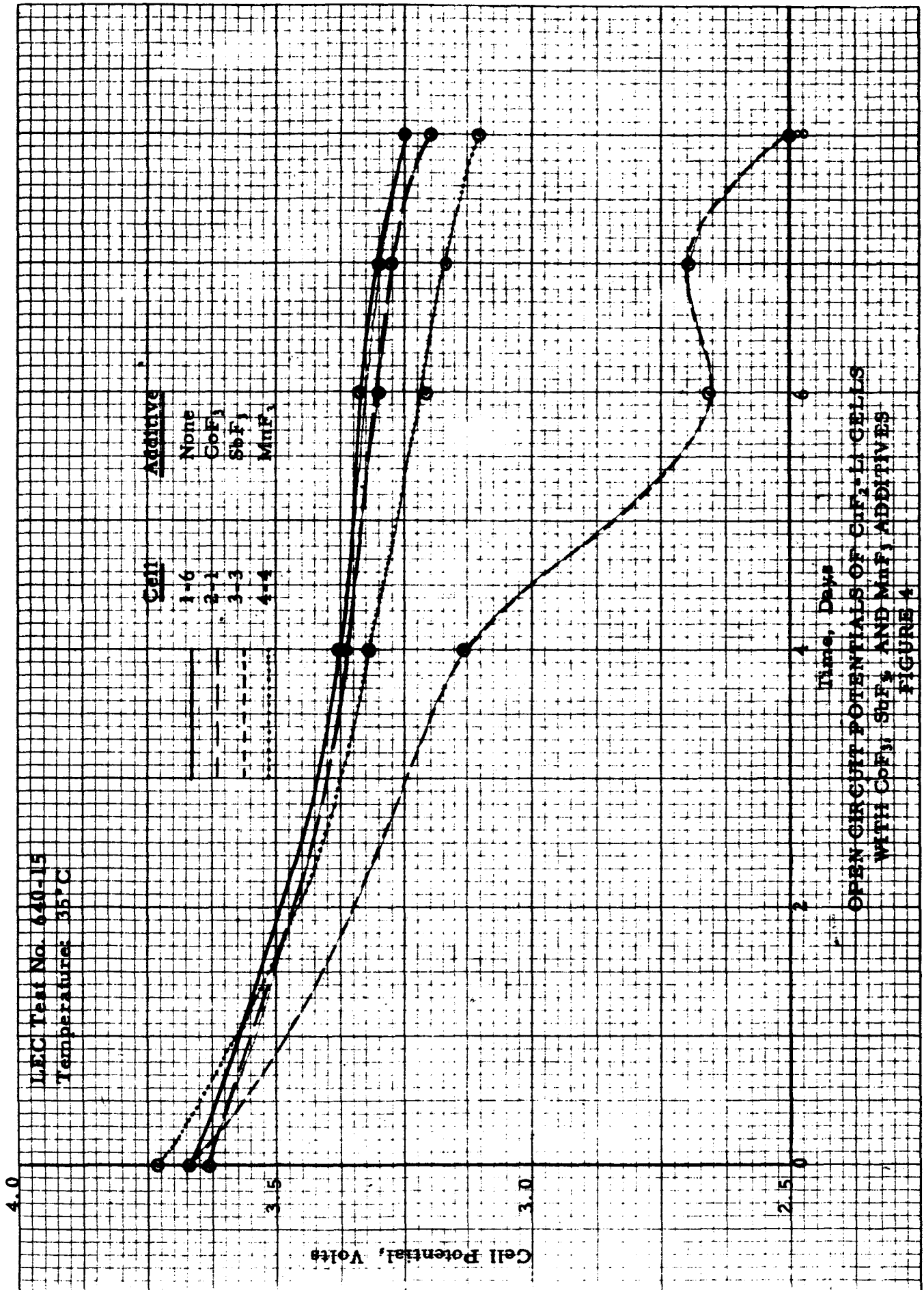
Cell No.	Additive	Grams Additive 100g CuF_2	Theo. CuF_2 Capacity, AH*	Stand Time at +35°C, days	Discharge Time to 2.5VF, hrs.	Average Disc. Potential, Volts	AH to 2.5VF	Cathode Eff. %
1-1	---	--	3.97	1	202	3.12	3.15	80
1-2	---	--	3.96	1	202	3.11	3.14	79
2-3	CoF_3	4	4.08	1	187	3.05	2.86	70
2-4	CoF_3	4	3.97	1	177	3.04	2.69	68
3-5	SbF_3	6	4.12	1	144	2.95	2.12	52
3-6	SbF_3	6	3.89	1	132	2.84	1.87	48
4-1	MnF_3	4	3.84	1	157	3.00	2.56	61
4-2	MnF_3	4	3.74	1	190	3.03	2.88	77
1-5	---	--	3.77	8	88	2.89	1.27	34
1-6	---	--	3.66	8	104	2.94	1.53	42
2-1	CoF_3	4	3.88	8	86	2.83	1.22	31
2-2	CoF_3	4	3.63	8	40	2.95	0.59	16
3-3	SbF_3	6	4.13	8	0	---	---	--
3-4	SbF_3	6	3.70	8	0	---	---	--
4-3	MnF_3	4	3.63	8	84	2.83	1.19	33
4-4	MnF_3	4	3.80	8	118	2.91	1.72	45
1-3	---	--	3.69	14	39	2.81	0.55	15
1-4	---	--	3.66	14	0	---	---	0
2-5	CoF_3	4	3.70	14	0	---	---	0
2-6	CoF_3	4	3.93	14	41	2.76	0.57	14
3-1	SbF_3	6	3.84	14	0	---	---	0
3-2	SbF_3	6	4.13	14	0	---	---	0
4-5	MnF_3	4	3.07	14	35	2.73	0.48	16
4-6	MnF_3	4	4.22	14	1	---	---	--

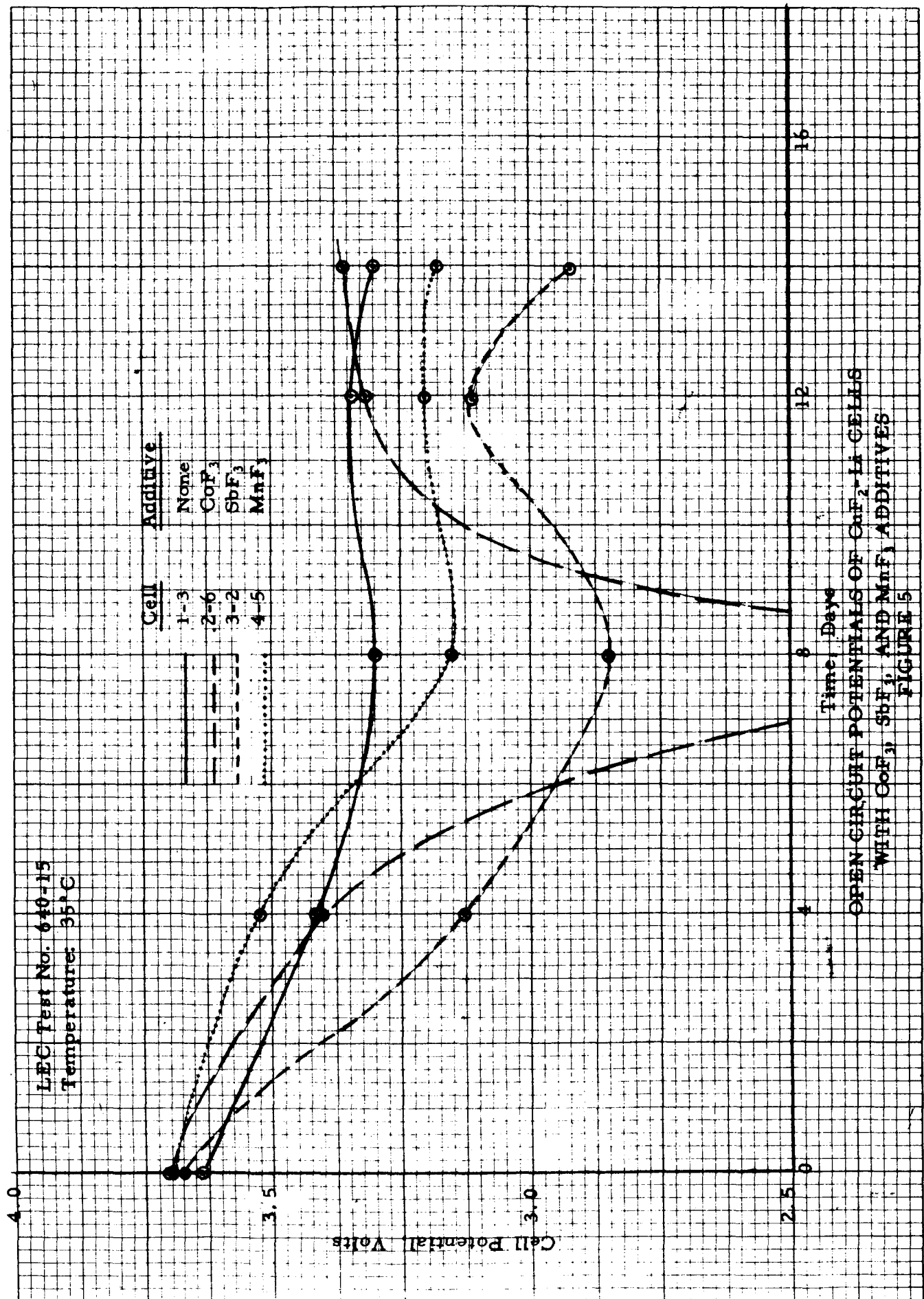
*Based on CuF_2 only.

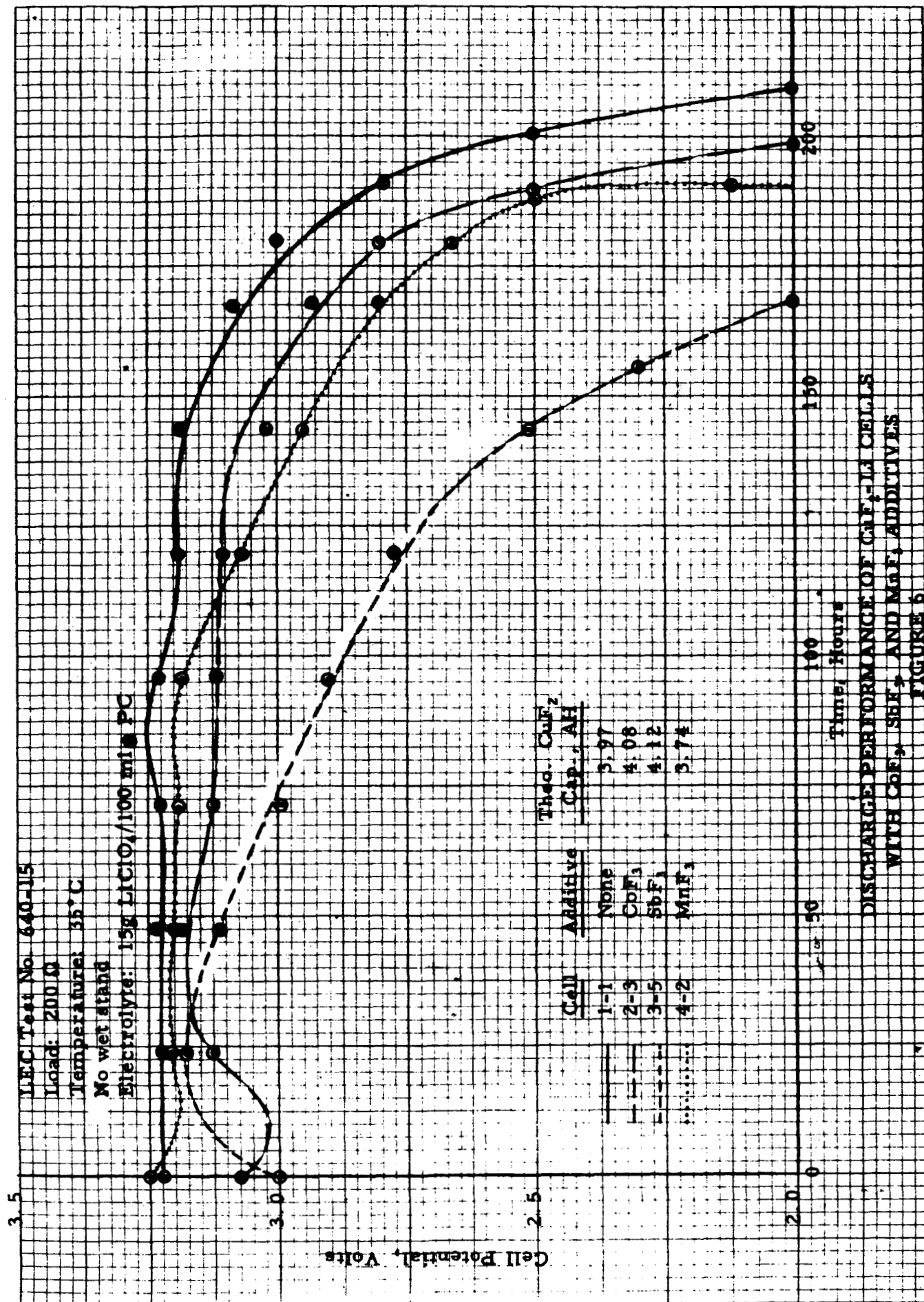
TABLE X
OPEN CIRCUIT POTENTIALS OF CuF_2 -Li CELLS CONTAINING ADDITIVES

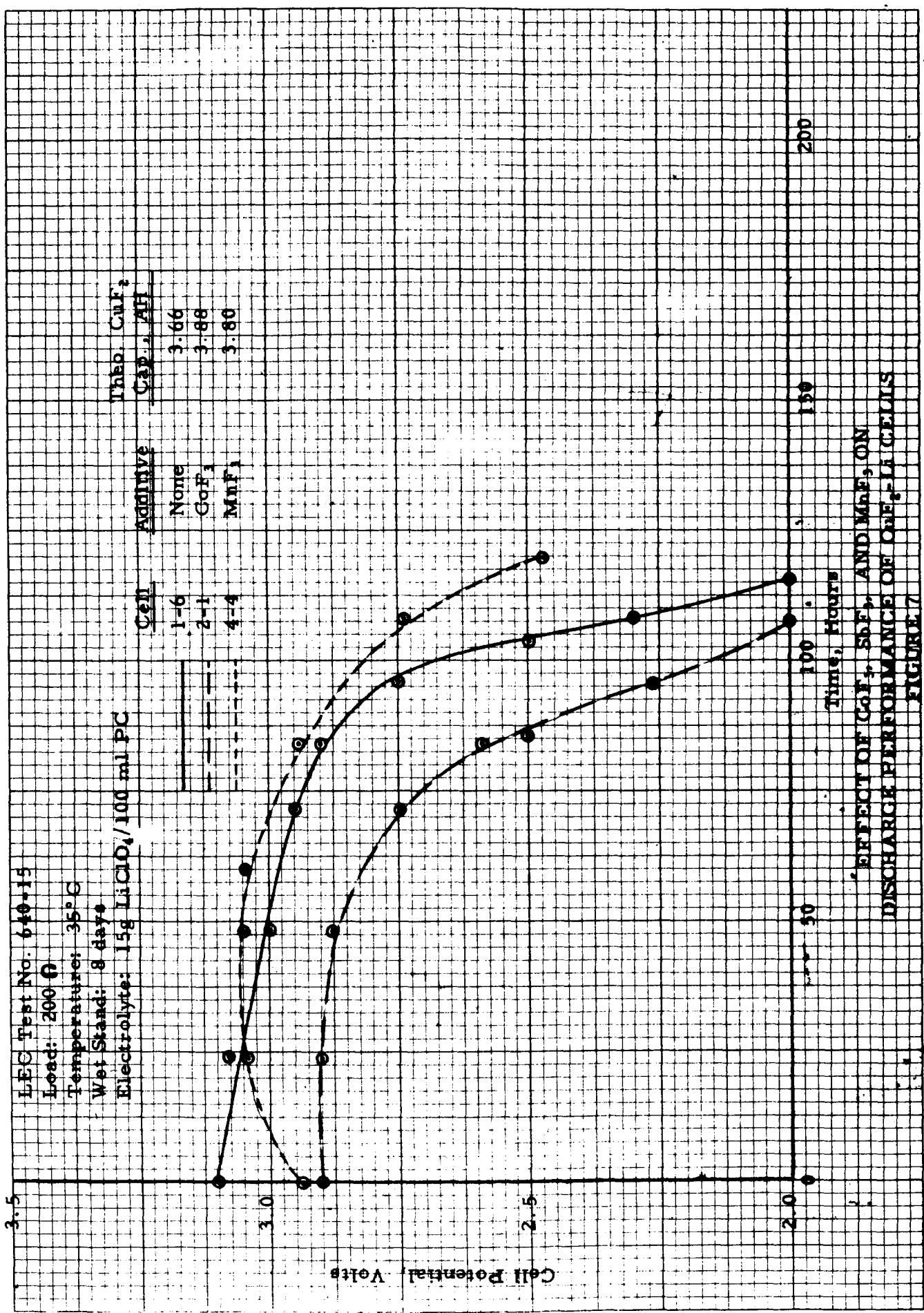
(LEC 640-15)

Cell No.	Additive	Open Circuit Potential												
		0 day	1 day	4 days	6 days	7 days	8 days	9 days	11 days	12 days	13 days	14 days		
1-1	---	3.69	3.63	---	---	---	---	---	---	---	---	---	---	---
1-2	---	3.68	3.64	---	---	---	---	---	---	---	---	---	---	---
2-3	CoF_3	3.73	3.71	---	---	---	---	---	---	---	---	---	---	---
2-4	CoF_3	3.74	3.71	---	---	---	---	---	---	---	---	---	---	---
3-5	SbF_3	3.68	3.58	---	---	---	---	---	---	---	---	---	---	---
3-6	SbF_3	3.68	3.61	---	---	---	---	---	---	---	---	---	---	---
4-1	MnF_3	3.74	3.66	---	---	---	---	---	---	---	---	---	---	---
4-2	MnF_3	3.74	3.67	---	---	---	---	---	---	---	---	---	---	---
1-5	---	3.69	---	3.35	3.35	3.35	3.30	---	---	---	---	---	---	---
1-6	---	3.67	---	3.38	3.34	3.30	3.25	---	---	---	---	---	---	---
2-1	CoF_3	3.63	---	3.37	3.30	3.28	3.20	---	---	---	---	---	---	---
2-2	CoF_3	3.71	---	3.42	3.32	3.22	3.30	---	---	---	---	---	---	---
3-3	SbF_3	3.67	---	3.13	2.66	2.70	2.50	---	---	---	---	---	---	---
3-4	SbF_3	3.67	---	3.21	2.80	2.61	2.35	---	---	---	---	---	---	---
4-3	MnF_3	3.72	---	3.31	3.24	3.26	3.20	---	---	---	---	---	---	---
4-4	MnF_3	3.73	---	3.32	3.21	3.17	3.10	---	---	---	---	---	---	---
1-3	---	3.64	---	3.41	3.33	3.31	3.30	3.27	3.36	3.34	3.30	3.30	3.30	3.30
1-4	---	3.65	---	3.42	3.30	3.24	3.05	3.08	3.01	3.03	2.27	1.63	1.63	1.63
2-5	CoF_3	3.73	---	3.38	3.30	3.30	3.20	3.18	3.10	2.99	2.85	2.59	2.59	2.59
2-6	CoF_3	3.71	---	3.40	3.23	3.01	0.85	2.92	3.36	3.31	3.28	3.35	3.35	3.35
3-1	SbF_3	3.67	---	3.19	2.63	2.94	2.85	3.03	2.48	2.32	2.18	2.02	2.02	2.02
3-2	SbF_3	3.67	---	3.13	2.88	2.87	2.85	2.98	3.11	3.11	3.02	2.92	2.92	2.92
4-5	MnF_3	3.70	---	3.53	3.25	3.20	3.15	3.08	3.14	3.21	3.13	3.18	3.18	3.18
4-6	MnF_3	3.70	---	3.34	3.17	3.13	3.15	3.17	3.27	3.27	3.23	3.28	3.28	3.28









3.3.2. Effect of LiClO_4 Concentration on Performance of Propylene Carbonate Cells

The effect of solute concentration on the solubility of CuF_2 in propylene carbonate-lithium perchlorate electrolytes has been studied previously (see NASA CR-54992, pages 10 to 14); in these tests, increasing the concentration of LiClO_4 caused higher solubility of CuF_2 in the electrolyte. During the past quarter, cell performance tests were conducted in order to establish a correlation between the results of the compatibility studies and cell performance, and to determine the optimum electrolyte concentration for the 100-1000 hour discharge rate CuF_2 -Li cells.

The positive electrodes were prepared by the standard filter mat technique and had the composition

CuF_2	100
Graphite	14
Paper Fiber	7.

Three-plate test cells with two lithium negative electrodes and 0.03 in. micro-porous rubber separation were constructed and assembled in groups of three cells in hermetically sealed jars.

Electrolyte solutions were prepared with lithium-dried and filtered propylene carbonate, and lithium perchlorate dried in vacuum at 110°C for 16 hours. The concentrations employed in this test were 10, 20, 30, and 40 grams of LiClO_4 per 100 milliliters of propylene carbonate.

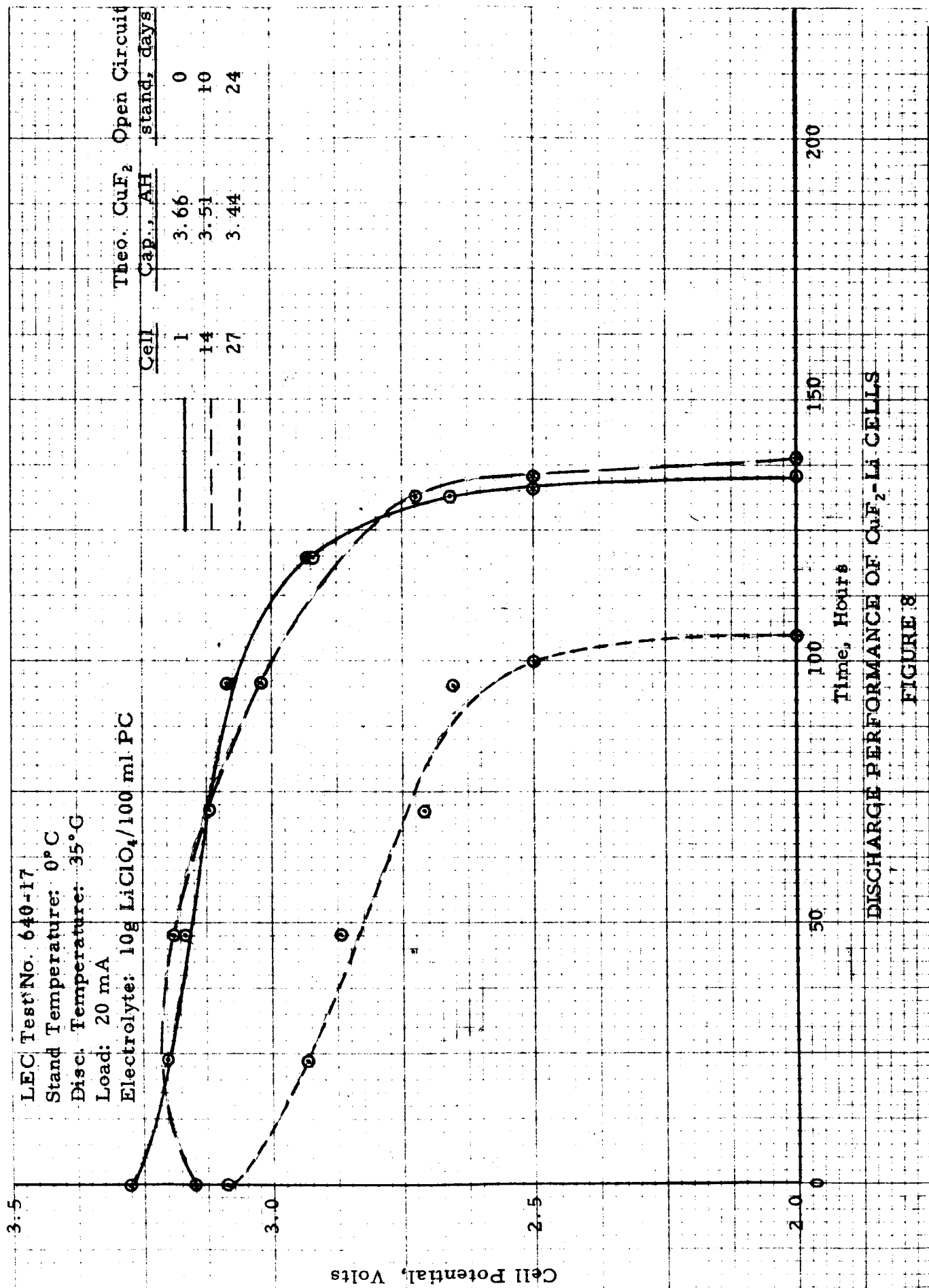
Construction and discharge data for the cells with 10 and 20 grams LiClO_4 per 100 ml PC are summarized in Table XI, page 33. Cells having the higher electrolyte concentrations showed very poor initial discharge performance (less than 12 hours to 2.5 VF at 20 mA and 35°C) and were discontinued from the test.

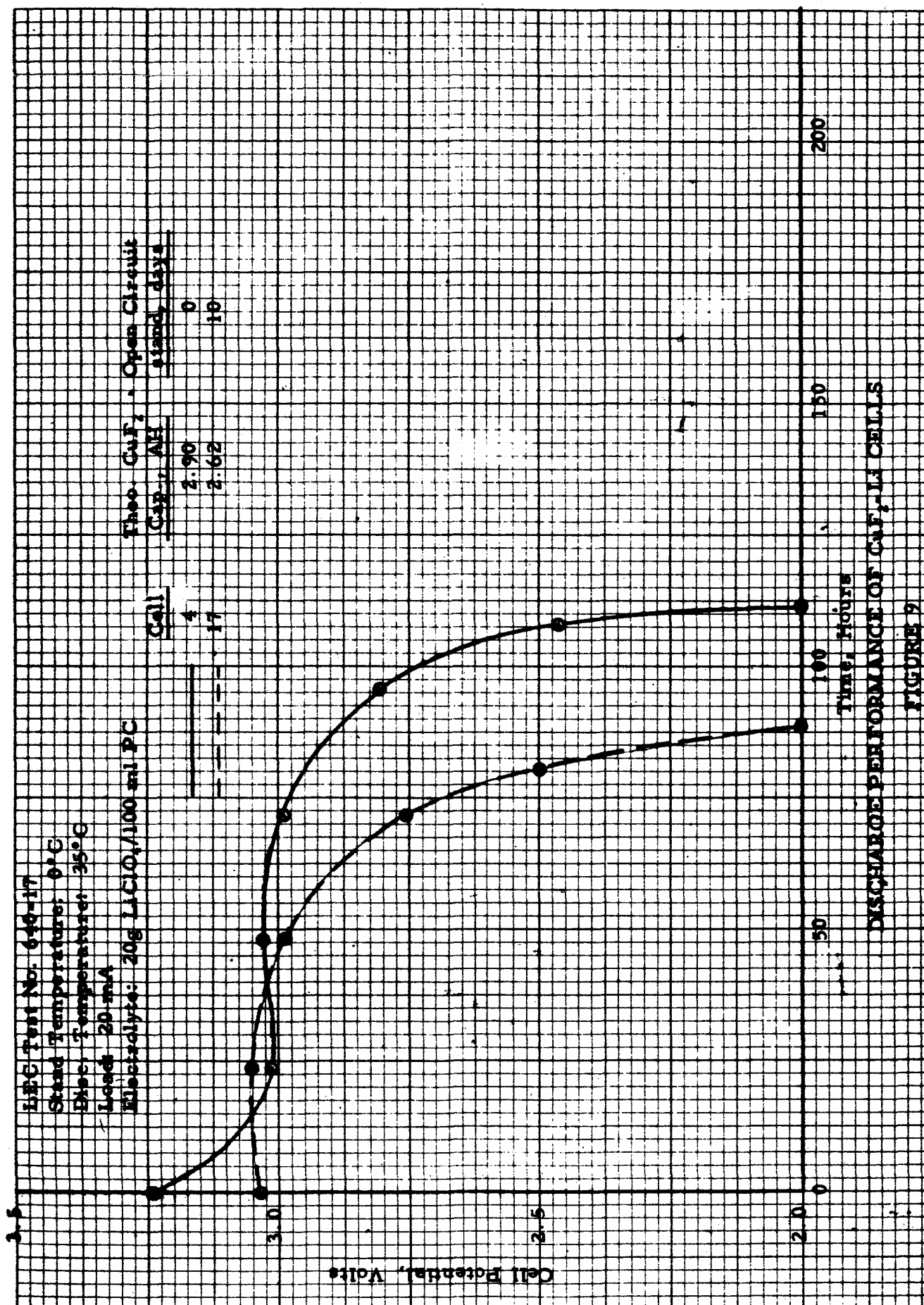
With no open circuit stand, capacity at the 20 mA (ca. 0.7 mA/cm^2) discharge rate at 35°C was about equal for both groups of cells. However, after 10 days of activated stand at 0°C , the CuF_2 reduction efficiency was 71, 73, and 77 percent for the three cells having the 10g/100 ml electrolyte, and 54, 60, and 62 percent for the cells having the 20g/100 ml solution. After 24 days of activated stand at 0°C , two of three cells with the lower electrolyte concentration retained capacity above 2.5 VF (58 and 19 percent reduction efficiency), while all three cells with the more concentrated electrolyte failed to give any capacity at this point. The discharge data for the best of three cells in each group before and after open circuit stand are presented in Figures 8 and 9, pages 34 and 35.

The results of this test indicate an improvement in wet shelf life with lower LiClO_4 concentration; this may be explained in terms of the lower solubility of CuF_2 in the less concentrated solution. Further cell tests with a range of more dilute electrolytes will be performed in order to identify the concentration which gives the best discharge and shelf life characteristics.

TABLE XI
PERFORMANCE OF CuF_2 -Li CELLS WITH LiClO_4 -PC ELECTROLYTE

Temperature: 35°C										
Cell No.	LiClO_4 conc. g/100 ml PC	Theo. CuF_2 Capacity, AH	Initial O. C. V.	Open circuit stand days at 0°C	Disc. Time to 2.5 VF hours	Average Disc.		AH 2.5 VF	Efficiency, %	
						Potential volts				
1	10	3.66	3.58	---	133	3.10		2.66	73	
2	10	3.06	3.58	---	79	2.91		1.58	52	
3	10	3.19	3.58	---	119	2.82		2.38	75	
4	20	2.90	3.55	---	108	2.96		2.16	75	
5	20	2.92	3.55	---	90	2.90		1.80	62	
6	20	3.21	3.55	---	120	2.93		2.40	75	
13	10	4.10	3.59	10	148.5	3.04		2.97	73	
14	10	3.51	3.59	10	135.5	3.04		2.71	77	
15	10	3.98	3.59	10	141	2.99		2.82	71	
16	20	3.80	3.50	10	100	2.82		2.00	54	
17	20	2.62	3.55	10	80.5	2.91		1.61	62	
18	20	2.58	3.55	10	87.5	2.95		1.75	60	
25	10	4.00	3.59	24	<1	---		---	---	
26	10	3.12	3.59	24	29.5	2.74		.59	19	
27	10	3.44	3.59	24	99.5	2.80		1.99	58	
28	20	2.87	3.59	24	<1	---		---	---	
29	20	3.71	3.58	24	<1	---		---	---	
30	20	3.68	3.35	24	<1	---		---	---	





3.3.3. Performance of CuF_2 -Li Cells at Various Discharge Rates

In order to further characterize the performance capabilities of the "low-rate" CuF_2 -Li system, discharge performance of cells having the usual filter-mat electrode construction (14 grams of graphite and 7 grams of paper fiber per 100 grams of CuF_2) was determined at various discharge loads. The electrolyte was 15g LiClO_4 /100 ml of propylene carbonate, and microporous rubber separation and slab lithium electrodes were employed as before. The geometric electrode area of the three-plate (1 CuF_2 electrode, 2 Li electrodes) cells was 29 cm^2 . Discharges were conducted at 35°C thru resistive loads of 100, 200, 500, and 1000 ohms. The construction and discharge data are summarized in Table XII, page 37, and voltage-time curves for the best cell at each discharge rate are presented in Figure 10, page 38.

In terms of CuF_2 reduction efficiency, the best performance was obtained from cells discharged thru 200 ohm loads (ca. 250 hour discharge); the highest reduction efficiency in this group (best of three cells) was 73 percent at an average discharge potential of 3.04V to a cut-off voltage of 2.5V. With 100 ohm loads (ca. 100 hour discharge), the best efficiency was 58 percent at 2.90V average discharge potential. With lower discharge rates, the performance again decreased, the best-of-three-cells figures being 47 percent efficiency at 3.20V average thru 500 ohm load (ca. 400 hour discharge), and 23 percent efficiency at 3.14V average thru 1000 ohm load (ca. 400 hour discharge).

Inspection of discharged cells showed copper-colored deposits on the lithium, particularly in the cells which were discharged thru 1000 ohm. Dissolution of CuF_2 was again evident in this test series, and probably contributed to the decreased performance of the cells with increasing discharge time. A means for minimizing the effect of dissolved copper must be developed before the present system can be utilized at either the longer discharge times, or where wet shelf life is required.

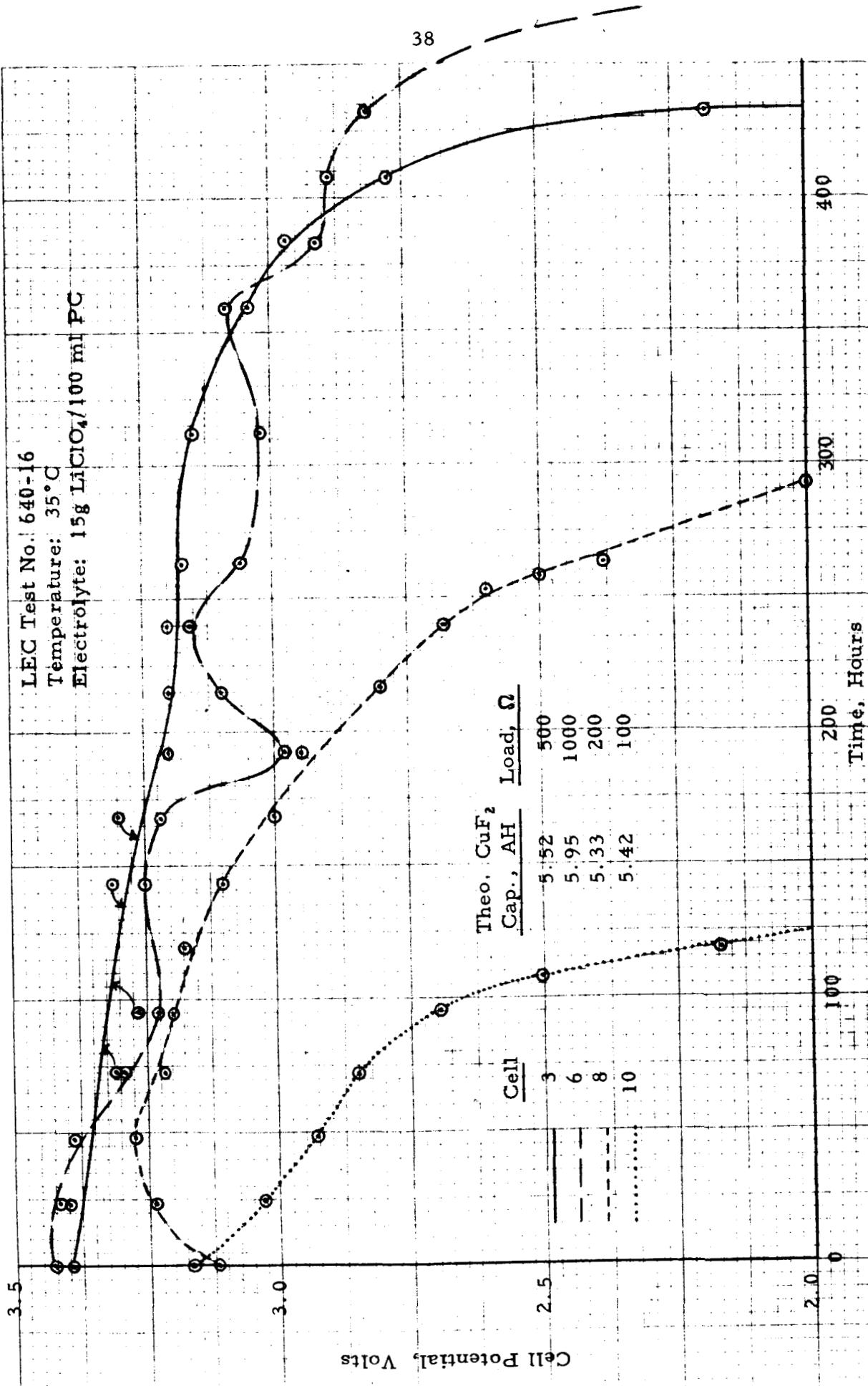
TABLE XII

PERFORMANCE OF CuF_2 -Li CELLS AT VARIOUS DISCHARGE RATES

(LEC Test No. 640-16)

<u>Cell No.</u>	<u>Theo. CuF_2 Capacity, AH</u>	<u>Load, Ω</u>	<u>Time to 2.5 VF, hrs.</u>	<u>Average Disc. Potentials, Volts</u>	<u>Capacity to 2.5VF, AH</u>	<u>Efficiency %</u>
1	5.67	500	432	3.14	2.68	47
2	5.92	500	360	3.07	2.21	37
3	5.52	500	408	3.20	2.62	47
4	6.13	1000	192	3.11	0.60	10
5	5.98	1000	360	3.18	1.14	19
6	5.95	1000	432	3.14	1.35	23
7	5.89	200	172	2.89	2.49	42
8	5.33	200	258	3.04	3.90	73
9	5.42	200	247	3.04	3.72	69
10	5.42	100	108	2.90	3.14	58
11	5.24	100	79	2.79	2.20	42
12	6.15	100	17	---	---	--

LEC Test No. 640-16
 Temperature: 35°C
 Electrolyte: 15g LiClO₄/100 ml PC



DISCHARGE PERFORMANCE OF CuF₂-LI CELLS
 AT VARIOUS DISCHARGE RATES
 FIGURE 10

4. APPENDIX

4. APPENDIX

4.1. Variance Analysis of Cell Discharge Data

The analysis of variance technique was applied to the data of Section 3.2.5.

The test was designed with three factors to be studied, graphite and paper concentrations and the effect of vacuum impregnation of the electrolyte into the cell.

To 50 grams of CuF_2 , graphite was added in amounts of 4, 8, and 16 grams, and paper in amounts of 2, 4, and 8 grams. Four cells were fabricated, two being activated by standard procedure and two using vacuum impregnation.

In the variance analysis, the four cells with equal graphite and paper concentrations were grouped together so that the factor of vacuum impregnation is not included in the analysis.

The measure of cell performance was taken to be the percent utilization of CuF_2 in the cathode.

The measure of the variance due to error was taken to be the sum of the squares within each cell.

Table XIII, page 43, shows the results of the variance analysis calculations up to the evaluation of the F ratio.

The final results of the variance analysis are given in Tables XIV and XV, page 44.

Table XIV lists the minimum mean square for a given level of significance of the respective mean square. These were calculated using the F ratio of the particular sample and the error mean square. Table XV lists the power of the F test for those values of F listed in Table XIII. This figure represents the percentage likelihood of rejecting the hypothesis that the particular groups have the same mean i. e. the same average cell efficiencies.

Since the mean square variation for both paper and graphite concentration (420 and 474) is less than the minimum mean square for significance at the 5 percent level (623), this would imply that neither paper concentration nor graphite concentration, as independent factors are directly related to cathode efficiency.

On the other hand, since the variance term due to graphite-paper interaction (1222) exceeds the mean square variation for the one (1) percent significance level the implication is that cell performance is more dependent upon the ratio of graphite to paper than on the concentration of either one of the components.

The data discussed above show that there is significant difference in cell efficiencies when the cathode composition is varied.

TABLE XIII
VARIANCE ANALYSIS CALCULATIONS

<u>Source of Variation</u>	<u>Degrees of Freedom</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>"F" Ratio</u>
Between paper pulp groups	2	840	420	2.26
Between graphite groups	2	948	474	2.54
Graphite/paper interaction	4	4888	1222	6.58
Error	27	5008	186	
TOTAL	35	11684		

TABLE XIV
MINIMUM MEAN SQUARE FOR STATISTICAL SIGNIFICANCE

Significance Level	<u>5%</u>	<u>1%</u>
Graphite Variation	623	1021
Paper Variation	623	1021
Graphite/Paper Interaction	508	765

TABLE XV
POWER OF THE F TEST

	<u>5%</u>	<u>1%</u>
Graphite Variation	65	38
Paper Variation	58	32
Graphite/Paper Interaction	97	88

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